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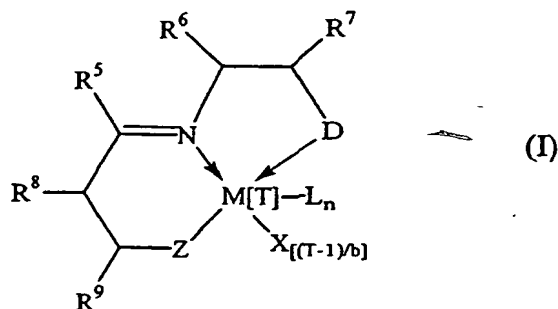
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(54) Title: NOVEL POLYMERISATION CATALYSTS



(57) Abstract: A complex, having the formula
(I) wherein M is a transition metal, lanthanide or
actinide and T is its oxidation state; X represents
an atom or group covalently or ionically bonded
to M; b is the valency of the atom or group X; L
is a group datively bound to M, and n is from 0 to
4; Z is oxygen, sulphur or a group represented by
NR¹⁰ or PR¹⁰; D is a group datively bound to M,
comprising a neutral donor selected from NR¹¹R¹²,
PR¹¹R¹², OR¹¹ or SR¹¹; and R⁵ to R¹² are hydrogen,
halogen, hydrocarbyl, substituted hydrocarbyl,
heterohydrocarbyl, substituted heterohydrocarbyl or

SiR₃, where each R' is hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl,
two or more of each R⁵ to R¹² may be linked to form cyclic substituents. Preferably R⁸ and R⁹ are linked to form a six-membered
carbon ring which is substituted by a cyclic hydrocarbyl group, preferably anthracenyl, naphthyl, triptycenyl or phenanthrenyl.
The complexes are useful as olefin (co)polymerisation catalysts.

WO 02/090365 A1

NOVEL POLYMERISATION CATALYSTS

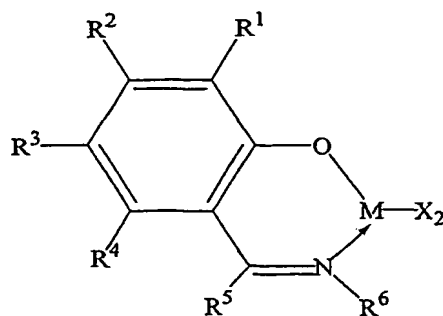
The present invention relates to novel polymerisation catalysts based on organic transition metal complexes and to a polymerisation process using the catalysts.

The use of certain transition metal compounds to polymerise 1-olefins, for example, ethylene, is well established in the prior art. The use of Ziegler-Natta catalysts, for example, those catalysts produced by activating titanium halides with organometallic compounds such as triethylaluminium, is fundamental to many commercial processes for manufacturing polyolefins. Over the last twenty or thirty years, advances in the technology have led to the development of Ziegler-Natta catalysts which have such high activities that olefin polymers and copolymers containing very low concentrations of residual catalyst can be produced directly in commercial polymerisation processes. The quantities of residual catalyst remaining in the produced polymer are so small as to render unnecessary their separation and removal for most commercial applications. Such processes can be operated by polymerising the monomers in the gas phase, or in solution or in suspension in a liquid hydrocarbon diluent. Polymerisation of the monomers can be carried out in the gas phase (the "gas phase process"), for example by fluidising under polymerisation conditions a bed comprising the target polyolefin powder and particles of the desired catalyst using a fluidising gas stream comprising the gaseous monomer. In the so-called "solution process" the (co)polymerisation is conducted by introducing the monomer into a solution or suspension of the catalyst in a liquid hydrocarbon diluent under conditions of temperature and pressure such that the produced polyolefin forms as a solution in the hydrocarbon diluent. In the "slurry process" the temperature, pressure and choice of

diluent are such that the produced polymer forms as a suspension in the liquid hydrocarbon diluent. These processes are generally operated at relatively low pressures (for example 10-50 bar) and low temperature (for example 50 to 150°C).

Commodity polyethylenes are commercially produced in a variety of different types and grades. Homopolymerisation of ethylene with transition metal based catalysts leads to the production of so-called "high density" grades of polyethylene. These polymers have relatively high stiffness and are useful for making articles where inherent rigidity is required. Copolymerisation of ethylene with higher 1-olefins (e.g. butene, hexene or octene) is employed commercially to provide a wide variety of copolymers differing in density and in other important physical properties. Particularly important copolymers made by copolymerising ethylene with higher 1-olefins using transition metal based catalysts are the copolymers having a density in the range of 0.91 to 0.93. These copolymers which are generally referred to in the art as "linear low density polyethylene" are in many respects similar to the so called "low density" polyethylene produced by the high pressure free radical catalysed polymerisation of ethylene. Such polymers and copolymers are used extensively in the manufacture of flexible blown film.

WO 98/42664 discloses as polymerisation catalysts compounds having the general Formula (0) shown below in which M is a transition metal and R¹ may be anthracenyl. EP 0874005A and WO 98/30609 also disclose compounds with similar generic formulas as Formula (0). Our own WO 99/19335 discloses such compounds where M is Cr, R¹ is t-Bu.



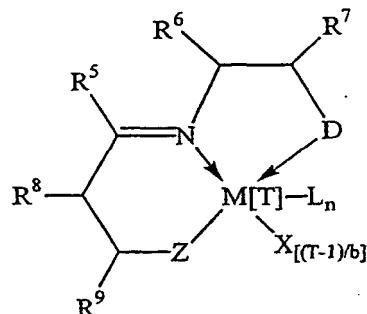
Formula (0)

An object of the present invention is to provide a novel complex and catalyst prepared therefrom suitable for polymerising olefins, and especially for polymerising ethylene alone or for copolymerising ethylene with higher 1-olefins. A further object of the invention is to provide an improved process for the polymerisation of olefins, especially of ethylene alone or the copolymerisation of ethylene with higher 1-olefins to

provide homopolymers and copolymers having controllable molecular weights. For example, using the catalyst of the present invention there can be made a wide variety of polyolefins such as, for example, liquid polyolefins, resinous or tacky polyolefins, solid polyolefins suitable for making flexible film and solid polyolefins having high stiffness.

5 We have discovered a class of novel transition metal complexes which have unexpectedly good activity as olefin polymerisation catalysts.

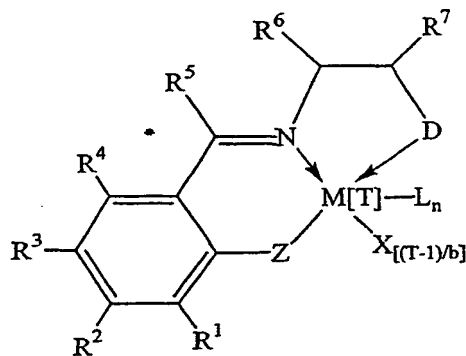
Accordingly, the present invention provides a complex having the formula (I)



Formula (I)

wherein M is a transition metal, lanthanide or actinide and T is its oxidation state; X represents an atom or group covalently or ionically bonded to M; b is the valency of the atom or group X; L is a group datively bound to M, and n is from 0 to 4; Z is oxygen, sulphur or a group represented by NR¹⁰ or PR¹⁰; D is a group datively bound to M, comprising a neutral donor selected from NR¹¹R¹², PR¹¹R¹², OR¹¹ or SR¹¹; and R⁵ to R¹² are all independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl or SiR'₃ where each R' is independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl, and any two or more of each R⁵ to R¹² may be linked to form cyclic substituents.

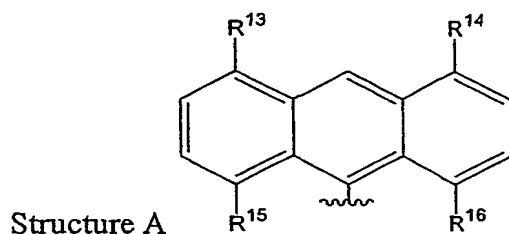
Preferably the complex of the invention has the formula (II)



20 Formula (II)

wherein R^5 to R^7 , M, T, L, n, b, X, Z and D are as defined above, and R^1 to R^4 are each independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl or SiR'_3 where each R' is independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl, and any two or more of R^1 to R^7 and R^{10} to R^{12} may be linked to form cyclic substituents.

Preferably R^1 is a cyclic hydrocarbyl group, more preferably R^1 is a polycyclic hydrocarbyl, and most preferably R^1 is anthracenyl, naphthyl, triptycenyl or phenanthrenyl, all of which may optionally be substituted, preferably with C_1 - C_6 alkyl groups. Thus, for example, the polycyclic hydrocarbyl group may be unsubstituted or substituted with one or more C_1 - C_6 alkyl groups and is preferably selected from anthracenyl, naphthyl, triptycenyl and phenanthrenyl. A particularly preferred group R^1 has the following Structure A:



where R^{13} to R^{16} are each independently hydrogen or methyl. Most preferably R^{13} to R^{16} are all hydrogen or R^{13} to R^{16} are all methyl.

Preferably M is Ti[II], Ti[III], Ti[IV], Fe[II], Fe[III], Co[II], Co[III], Ni[II], Cr[II], Cr[III], Mn[II], Mn[III], Mn[IV], Ta[II], Ta[III], Ta[IV], Rh[II], Rh[III], Y[II], Y[III], Sc[II], Sc[III], Ru[II], Ru[III], Ru[IV], Pd[II], Zr[II], Zr[III], Zr[IV], Hf[II], Hf[III], Hf[IV], V[II], V[III], V[IV], Nb[II], Nb[III], Nb[IV] or Nb[V].

More preferably M is Ti[II], Ti[III], Ti[IV], Ta[II], Ta[III], Ta[IV], Zr[II], Zr[III], Zr[IV], Hf[II], Hf[III], Hf[IV], V[II], V[III], V[IV], Nb[II], Nb[III], Nb[IV] or Nb[V].

Most preferably M is Ti[III] or Ti[IV].

Preferably Z is oxygen.

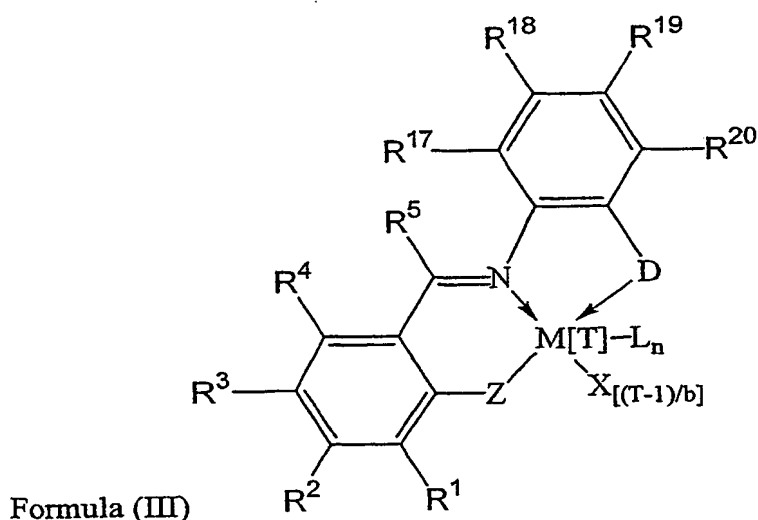
Where D is $PR^{11}R^{12}$ then preferably R^{11} and R^{12} are both phenyl. Preferably D is $NR^{11}R^{12}$ where R^{11} and R^{12} are as defined above. More preferably R^{11} and R^{12} are each independently a hydrogen or hydrocarbyl group.

- The atom or group represented by X in the complexes of Formula (I) or (II) can be, for example, selected from halide, sulphate, nitrate, thiolate, thiocarboxylate, BF_4^- , PF_6^- , hydride, hydrocarbyloxy, carboxylate, hydrocarbyl, substituted hydrocarbyl and heterohydrocarbyl, β -diketonates, or mixtures thereof. Preferably the atoms or groups
- 5 X are halide, for example, chloride, bromide; hydride; hydrocarbyloxy, for example, methoxide, ethoxide, isopropoxide, phenoxide; carboxylate, for example, formate, acetate, benzoate; hydrocarbyl, for example, methyl, ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl; substituted hydrocarbyl; heterohydrocarbyl; tosylate; or triflate. More preferably X is selected from halide, hydride, hydrocarbyloxy and hydrocarbyl.
- 10 Chloride, isopropoxide or mixtures thereof are particularly preferred.

The group L may be an ether, such as tetrahydrofuran or diethylether; an alcohol such as ethanol or butanol; a primary, secondary or tertiary amine; or a phosphine.

- In one preferred embodiment of the present invention R^2 to R^7 are all independently selected from hydrogen or hydrocarbyl. In this embodiment the most
- 15 preferable complex is of the Formula (II), above, where M is Ti(IV), Z is oxygen, R^1 is Structure A, all of R^2 to R^7 are hydrogen, R^{13} to R^{16} are all methyl and D is NMe_2 , the three X groups consist of 2 Cl groups and one O^iPr group, and L is tetrahydrofuran.

- Alternatively, in a second preferred embodiment, at least two of R^2 to R^7 are linked to form a cyclic substituent. Preferably R^6 and R^7 are linked to form a cyclic
- 20 substituent, forming a complex of the Formula (III), below:



wherein R^1 to R^5 , M, T, L, n, b, X, Z and D are as defined above, and R^{17} to R^{20} are each independently selected from hydrogen, halogen, hydrocarbyl, substituted

hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl or SiR'_3 where each R' is independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl, and any two or more of the R groups may be linked to form cyclic substituents. Preferably R^2 to R^5 and/or R^{17} to R^{20} are each independently selected from hydrogen or hydrocarbyl. In the most preferable complex of this second embodiment M is Ti(IV), Z is oxygen, R^1 is Structure A, R^2 to R^5 and R^{13} to R^{20} are all hydrogen and D is NHPH, the three X groups consist of 2 Cl groups and one O^iPr group, and L is tetrahydrofuran.

- A second aspect of the invention provides a polymerisation catalyst comprising
- 10 a) a complex as defined above, and, optionally,
 - b) an effective amount of at least one activator compound.

The activator compound for the catalyst of the present invention, when required, is suitably selected from organoaluminium compounds and hydrocarbylboron compounds. Suitable organoaluminium compounds include compounds of the formula

15 AlR_3 , where each R is independently C_1 - C_{12} alkyl or halo. Examples include trimethylaluminium (TMA), triethylaluminium (TEA), tri-isobutylaluminium (TIBA), tri-n-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium chloride, diethylaluminium chloride, ethylaluminiumsesquichloride, methylaluminiumsesquichloride, and alumoxanes. Alumoxanes are well known in the

20 art as typically the oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic or mixtures thereof. Commercially available alumoxanes are generally believed to be mixtures of linear and cyclic compounds. The cyclic alumoxanes can be represented by the formula $[\text{R}^{21}\text{AlO}]_s$ and the linear

25 alumoxanes by the formula $\text{R}^{22}(\text{R}^{23}\text{AlO})_s$ wherein s is a number from about 2 to 50, and wherein R^{21} , R^{22} , and R^{23} represent hydrocarbyl groups, preferably C_1 to C_6 alkyl groups, for example methyl, ethyl or butyl groups. Alkylalumoxanes such as methylalumoxane (MAO) are preferred.

Mixtures of alkylalumoxanes and trialkylaluminium compounds are particularly

30 preferred, such as MAO with TMA or TIBA. In this context it should be noted that the term "alkylalumoxane" as used in this specification includes alkylalumoxanes available commercially which may contain a proportion, typically about 10wt%, but optionally up

to 50wt%, of the corresponding trialkylaluminium; for instance, commercial MAO usually contains approximately 10wt% trimethylaluminium (TMA), whilst commercial MMAO contains both TMA and TIBA. Quantities of alkylalumoxane quoted herein include such trialkylaluminium impurities, and accordingly quantities of

5 trialkylaluminium compounds quoted herein are considered to comprise compounds of the formula AlR_3 additional to any AlR_3 compound incorporated within the alkylalumoxane when present.

Examples of suitable hydrocarbylboron compounds are boroxines, trimethylboron, triethylboron, dimethylphenylammoniumtetra(phenyl)borate,

10 trityltetra(phenyl)borate, triphenylboron, dimethylphenylammonium tetra(pentafluorophenyl)borate, sodium tetrakis[(bis-3,5-trifluoromethyl)phenyl]borate, $H^+(OEt_2)[(bis-3,5-trifluoromethyl)phenyl]borate$, trityltetra(pentafluorophenyl)borate and tris(pentafluorophenyl) boron.

In the preparation of the catalysts of the present invention the quantity of

15 activating compound selected from organoaluminium compounds and hydrocarbylboron compounds to be employed is easily determined by simple testing, for example, by the preparation of small test samples which can be used to polymerise small quantities of the monomer(s) and thus to determine the activity of the produced catalyst. It is generally found that the quantity employed is sufficient to provide 0.1 to 20,000 atoms,

20 preferably 1 to 2000 atoms of aluminium or boron per atom of metal in the transition metal compound.

An alternative class of activators comprise salts of a cationic oxidising agent and a non-coordinating compatible anion. Examples of cationic oxidising agents include: ferrocenium, hydrocarbyl-substituted ferrocenium, Ag^+ , or Pb^{2+} . Examples of non-

25 coordinating compatible anions are BF_4^- , $SbCl_6^-$, PF_6^- , tetrakis(phenyl)borate and tetrakis(pentafluorophenyl)borate.

The polymerisation catalyst of the present invention may also comprise (3) a neutral Lewis base.

Neutral Lewis bases are well known in the art of Ziegler-Natta catalyst

30 polymerisation technology. Examples of classes of neutral Lewis bases suitably employed in the present invention are unsaturated hydrocarbons, for example, alkenes (other than 1-olefins) or alkynes, primary, secondary and tertiary amines, amides,

phosphoramides, phosphines, phosphites, ethers, thioethers, nitriles, carbonyl compounds, for example, esters, ketones, aldehydes, carbon monoxide and carbon dioxide, sulphoxides, sulphones and boroxines. Although 1-olefins are capable of acting as neutral Lewis bases, for the purposes of the present invention they are regarded as monomer or comonomer 1-olefins and not as neutral Lewis bases *per se*. However, alkenes which are internal olefins, for example, 2-butene and cyclohexene are regarded as neutral Lewis bases in the present invention. Preferred Lewis bases are tertiary amines and aromatic esters, for example, dimethylaniline, diethylaniline, tributylamine, ethylbenzoate and benzylbenzoate. In this particular aspect of the present invention, components (1), (2) and (3) of the catalyst system can be brought together simultaneously or in any desired order. However, if components (2) and (3) are compounds which interact together strongly, for example, form a stable compound together, it is preferred to bring together either components (1) and (2) or components (1) and (3) in an initial step before introducing the final defined component. Preferably components (1) and (3) are contacted together before component (2) is introduced. The quantities of components (1) and (2) employed in the preparation of this catalyst system are suitably as described above in relation to the catalysts of the present invention. The quantity of the neutral Lewis Base [component (3)] is preferably such as to provide a ratio of component (1):component (3) in the range 100:1 to 1:1000, most preferably in the range 1:1 to 1:20. Components (1), (2) and (3) of the catalyst system can be brought together, for example, as the neat materials, as a suspension or solution of the materials in a suitable diluent or solvent (for example a liquid hydrocarbon), or, if at least one of the components is volatile, by utilising the vapour of that component. The components can be brought together at any desired temperature. Mixing the components together at room temperature is generally satisfactory. Heating to higher temperatures e.g. up to 120°C can be carried out if desired, e.g. to achieve better mixing of the components. It is preferred to carry out the bringing together of components (1), (2) and (3) in an inert atmosphere (e.g. dry nitrogen) or *in vacuo*. If it is desired to use the catalyst on a support material (see below), this can be achieved, for example, by preforming the catalyst system comprising components (1), (2) and (3) and impregnating the support material preferably with a solution thereof, or by introducing to the support material one or more of the components simultaneously or sequentially. If desired the support

material itself can have the properties of a neutral Lewis base and can be employed as, or in place of, component (3). An example of a support material having neutral Lewis base properties is poly(aminostyrene) or a copolymer of styrene and aminostyrene (i.e. vinylaniline).

5 The catalysts of the present invention can if desired comprise more than one of the defined complexes. Alternatively, the catalysts of the present invention can also include one or more other types of transition metal compounds or catalysts, for example, nitrogen containing catalysts such as those described in WO 99/12981. Examples of such other catalysts include 2,6-diacetylpyridinebis(2,4,6-trimethyl anil)FeCl₂.

10 The catalysts of the present invention can also include one or more other types of catalyst, such as those of the type used in conventional Ziegler-Natta catalyst systems, metallocene-based catalysts, monocyclopentadienyl- or constrained geometry based catalysts, or heat activated supported chromium oxide catalysts (e.g. Phillips-type catalyst).

15 The catalysts of the present invention can be unsupported or supported on a support material, for example, silica, alumina, MgCl₂ or zirconia, or on a polymer or prepolymer, for example polyethylene, polypropylene, polystyrene, or poly(aminostyrene).

20 If desired the catalysts can be formed in situ in the presence of the support material, or the support material can be pre-impregnated or premixed, simultaneously or sequentially, with one or more of the catalyst components. The catalysts of the present invention can if desired be supported on a heterogeneous catalyst, for example, a magnesium halide supported Ziegler Natta catalyst, a Phillips type (chromium oxide) supported catalyst or a supported metallocene catalyst. Formation of the supported catalyst can be achieved for example by treating the transition metal complexes of the present invention with alumoxane in a suitable inert diluent, for example a volatile hydrocarbon, slurring a particulate support material with the product and evaporating the volatile diluent. The produced supported catalyst is preferably in the form of a free-flowing powder. The quantity of support material employed can vary widely, for example from 100,000 to 1 grams per gram of metal present in the transition metal complex.

30

Alternatively the precursor components of the catalyst may be added directly to

the polymerisation reactor together with the 1-olefin to be polymerised.

The present invention further provides a process for the polymerisation and copolymerisation of 1-olefins, comprising contacting the monomeric olefin under polymerisation conditions with the polymerisation catalyst of the present invention. A preferred process comprises the steps of :

- a) preparing a prepolymer-based catalyst by contacting one or more 1-olefins with a catalyst system, and
- b) contacting the prepolymer-based catalyst with one or more 1-olefins, wherein the catalyst system is as defined above.

In the text herein below, the term "catalyst" is intended to include "prepolymer-based catalyst" as defined above.

The polymerisation conditions can be, for example, solution phase, slurry phase, gas phase or bulk phase, with polymerisation temperatures ranging from -100°C to +300°C, and at pressures of atmospheric and above, particularly from 140 to 4100 kPa.

If desired, the catalyst can be used to polymerise ethylene under high pressure/high temperature process conditions wherein the polymeric material forms as a melt in supercritical ethylene. Preferably the polymerisation is conducted under gas phase fluidised bed or stirred bed conditions.

Suitable monomers for use in the polymerisation process of the present invention are, for example, ethylene and C₃₋₂₀ α-olefins, specifically propylene, 1-butene, 1-pentene, 1-hexene, 4-methylpentene-1, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, and 1-eicosene. Other monomers include methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, and styrene. Preferred monomers for homopolymerisation processes are ethylene and propylene.

The catalysts and process of the invention can also be used for copolymerising ethylene or propylene with each other or with other 1-olefins such as 1-butene, 1-hexene, 4-methylpentene-1, and octene, or with other monomeric materials, for example, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, and styrene. Polymerisation of 1-olefins with dienes, particularly non-conjugated dienes, such as 1,4 pentadiene, 1,5-hexadiene, cyclopentadiene and ethylene

norbornadiene is also possible. In particular, ethylene/1-olefin/diene terpolymers may be made by the process of the invention where the diene is as above and the other 1-olefin is preferably propylene.

Irrespective of the polymerisation or copolymerisation technique employed, polymerisation or copolymerisation is typically carried out under conditions that substantially exclude oxygen, water, and other materials that act as catalyst poisons. Also, polymerisation or copolymerisation can be carried out in the presence of additives to control polymer or copolymer molecular weights.

The use of hydrogen gas as a means of controlling the average molecular weight of the polymer or copolymer applies generally to the polymerisation process of the present invention. For example, hydrogen can be used to reduce the average molecular weight of polymers or copolymers prepared using gas phase, slurry phase, bulk phase or solution phase polymerisation conditions. The quantity of hydrogen gas to be employed to give the desired average molecular weight can be determined by simple "trial and error" polymerisation tests.

The polymerisation process of the present invention provides polymers and copolymers, especially ethylene polymers, at remarkably high productivity (based on the amount of polymer or copolymer produced per unit weight of complex employed in the catalyst system). This means that relatively very small quantities of transition metal complex are consumed in commercial processes using the process of the present invention. It also means that when the polymerisation process of the present invention is operated under polymer recovery conditions that do not employ a catalyst separation step, thus leaving the catalyst, or residues thereof, in the polymer (e.g. as occurs in most commercial slurry and gas phase polymerisation processes), the amount of transition metal complex in the produced polymer can be very small.

Slurry phase polymerisation conditions or gas phase polymerisation conditions are particularly useful for the production of high or low density grades of polyethylene, and polypropylene. In these processes the polymerisation conditions can be batch, continuous or semi-continuous. Furthermore, one or more reactors may be used, e.g. from two to five reactors in series. Different reaction conditions, such as different temperatures or hydrogen concentrations may be employed in the different reactors. In the slurry phase process and the gas phase process, the catalyst is generally metered and

transferred into the polymerisation zone in the form of a particulate solid either as a dry powder (e.g. with an inert gas) or as a slurry. This solid can be, for example, a solid catalyst system formed from the one or more of complexes of the invention and an activator with or without other types of catalysts, or can be the solid catalyst alone with or without other types of catalysts. In the latter situation, the activator can be fed to the polymerisation zone, for example as a solution, separately from or together with the solid catalyst. Preferably the catalyst system or the transition metal complex component of the catalyst system employed in the slurry polymerisation and gas phase polymerisation is supported on one or more support materials. Most preferably the catalyst system is supported on the support material prior to its introduction into the polymerisation zone. Suitable support materials are, for example, silica, alumina, zirconia, talc, kieselguhr, or magnesia. Impregnation of the support material can be carried out by conventional techniques, for example, by forming a solution or suspension of the catalyst components in a suitable diluent or solvent, and slurrying the support material therewith. The support material thus impregnated with catalyst can then be separated from the diluent for example, by filtration or evaporation techniques. Once the polymer product is discharged from the reactor, any associated and absorbed hydrocarbons are substantially removed, or degassed, from the polymer by, for example, pressure let-down or gas purging using fresh or recycled steam, nitrogen or light hydrocarbons (such as ethylene). Recovered gaseous or liquid hydrocarbons may be recycled to the polymerisation zone.

In the slurry phase polymerisation process the solid particles of catalyst, or supported catalyst, are fed to a polymerisation zone either as dry powder or as a slurry in the polymerisation diluent. The polymerisation diluent is compatible with the polymer(s) and catalyst(s), and may be an alkane such as hexane, heptane, isobutane, or a mixture of hydrocarbons or paraffins. Preferably the particles are fed to a polymerisation zone as a suspension in the polymerisation diluent. The polymerisation zone can be, for example, an autoclave or similar reaction vessel, or a continuous loop reactor, e.g. of the type well-known in the manufacture of polyethylene by the Phillips Process. When the polymerisation process of the present invention is carried out under slurry conditions the polymerisation is preferably carried out at a temperature above 0°C, most preferably above 15°C. The polymerisation temperature is preferably

maintained below the temperature at which the polymer commences to soften or sinter in the presence of the polymerisation diluent. If the temperature is allowed to go above the latter temperature, fouling of the reactor can occur. Adjustment of the polymerisation within these defined temperature ranges can provide a useful means of controlling the average molecular weight of the produced polymer. A further useful means of controlling the molecular weight is to conduct the polymerisation in the presence of hydrogen gas which acts as chain transfer agent. Generally, the higher the concentration of hydrogen employed, the lower the average molecular weight of the produced polymer.

10 In bulk polymerisation processes, liquid monomer such as propylene is used as the polymerisation medium.

Methods for operating gas phase polymerisation processes are well known in the art. Such methods generally involve agitating (e.g. by stirring, vibrating or fluidising) a bed of catalyst, or a bed of the target polymer (i.e. polymer having the same or similar physical properties to that which it is desired to make in the polymerisation process) containing a catalyst, and feeding thereto a stream of monomer at least partially in the gaseous phase, under conditions such that at least part of the monomer polymerises in contact with the catalyst in the bed. The bed is generally cooled by the addition of cool gas (e.g. recycled gaseous monomer) and/or volatile liquid (e.g. a volatile inert hydrocarbon, or gaseous monomer which has been condensed to form a liquid). The polymer produced in, and isolated from, gas phase processes forms directly a solid in the polymerisation zone and is free from, or substantially free from liquid. As is well known to those skilled in the art, if any liquid is allowed to enter the polymerisation zone of a gas phase polymerisation process the quantity of liquid in the polymerisation zone is small in relation to the quantity of polymer present.. This is in contrast to "solution phase" processes wherein the polymer is formed dissolved in a solvent, and "slurry phase" processes wherein the polymer forms as a suspension in a liquid diluent.

The gas phase process can be operated under batch, semi-batch, or so-called "continuous" conditions. It is preferred to operate under conditions such that monomer is continuously recycled to an agitated polymerisation zone containing polymerisation catalyst, make-up monomer being provided to replace polymerised monomer, and continuously or intermittently withdrawing produced polymer from the polymerisation

zone at a rate comparable to the rate of formation of the polymer, fresh catalyst being added to the polymerisation zone to replace the catalyst withdrawn from the polymerisation zone with the produced polymer.

For typical production of impact copolymers, homopolymer formed from the first monomer in a first reactor is reacted with the second monomer in a second reactor. For manufacture of propylene/ethylene impact copolymer in a gas-phase process, propylene is polymerized in a first reactor; reactive polymer transferred to a second reactor in which ethylene or other comonomer is added. The result is an intimate mixture of a isotactic polypropylene chains with chains of a random propylene/ethylene copolymer. A random copolymer typically is produced in a single reactor in which a minor amount of a comonomer (typically ethylene) is added to polymerizing chains of propylene.

Methods for operating gas phase fluidised bed processes for making polyethylene, ethylene copolymers and polypropylene are well known in the art. The process can be operated, for example, in a vertical cylindrical reactor equipped with a perforated distribution plate to support the bed and to distribute the incoming fluidising gas stream through the bed. The fluidising gas circulating through the bed serves to remove the heat of polymerisation from the bed and to supply monomer for polymerisation in the bed. Thus the fluidising gas generally comprises the monomer(s) normally together with some inert gas (e.g. nitrogen or inert hydrocarbons such as methane, ethane, propane, butane, pentane or hexane) and optionally with hydrogen as molecular weight modifier. The hot fluidising gas emerging from the top of the bed is led optionally through a velocity reduction zone (this can be a cylindrical portion of the reactor having a wider diameter) and, if desired, a cyclone and or filters to disentrain fine solid particles from the gas stream. The hot gas is then led to a heat exchanger to remove at least part of the heat of polymerisation. Catalyst is preferably fed continuously or at regular intervals to the bed. At start up of the process, the bed comprises fluidisable polymer which is preferably similar to the target polymer. Polymer is produced continuously within the bed by the polymerisation of the monomer(s). Preferably means are provided to discharge polymer from the bed continuously or at regular intervals to maintain the fluidised bed at the desired height. The process is generally operated at relatively low pressure, for example, at 10 to 50 bars, and at temperatures for example, between 50 and 120 °C. The temperature of the bed is maintained below

the sintering temperature of the fluidised polymer to avoid problems of agglomeration.

In the gas phase fluidised bed process for polymerisation of olefins the heat evolved by the exothermic polymerisation reaction is normally removed from the polymerisation zone (i.e. the fluidised bed) by means of the fluidising gas stream as described above. The hot reactor gas emerging from the top of the bed is led through one or more heat exchangers wherein the gas is cooled. The cooled reactor gas, together with any make-up gas, is then recycled to the base of the bed. In the gas phase fluidised bed polymerisation process of the present invention it is desirable to provide additional cooling of the bed (and thereby improve the space time yield of the process) by feeding a volatile liquid to the bed under conditions such that the liquid evaporates in the bed thereby absorbing additional heat of polymerisation from the bed by the "latent heat of evaporation" effect. When the hot recycle gas from the bed enters the heat exchanger, the volatile liquid can condense out. In one embodiment of the present invention the volatile liquid is separated from the recycle gas and reintroduced separately into the bed. Thus, for example, the volatile liquid can be separated and sprayed into the bed. In another embodiment of the present invention the volatile liquid is recycled to the bed with the recycle gas. Thus the volatile liquid can be condensed from the fluidising gas stream emerging from the reactor and can be recycled to the bed with recycle gas, or can be separated from the recycle gas and then returned to the bed.

The method of condensing liquid in the recycle gas stream and returning the mixture of gas and entrained liquid to the bed is described in EP-A-0089691 and EP-A-0241947. It is preferred to reintroduce the condensed liquid into the bed separate from the recycle gas using the process described in our US Patent 5541270, the teaching of which is hereby incorporated into this specification.

When using the catalysts of the present invention under gas phase polymerisation conditions, the catalyst, or one or more of the components employed to form the catalyst can, for example, be introduced into the polymerisation reaction zone in liquid form, for example, as a solution in an inert liquid diluent. Thus, for example, the transition metal component, or the activator component, or both of these components can be dissolved or slurried in a liquid diluent and fed to the polymerisation zone. Under these circumstances it is preferred the liquid containing the component(s) is sprayed as fine droplets into the polymerisation zone. The droplet diameter is preferably within the

range 1 to 1000 microns. EP-A-0593083, the teaching of which is hereby incorporated into this specification, discloses a process for introducing a polymerisation catalyst into a gas phase polymerisation. The methods disclosed in EP-A-0593083 can be suitably employed in the polymerisation process of the present invention if desired.

5 Although not usually required, upon completion of polymerisation or copolymerisation, or when it is desired to terminate polymerisation or copolymerisation or at least temporarily deactivate the catalyst or catalyst component of this invention, the catalyst can be contacted with water, alcohols, acetone, or other suitable catalyst deactivators a manner known to persons of skill in the art.

10 Homopolymerisation of ethylene with the catalysts of the invention may produce so-called "high density" grades of polyethylene. These polymers have relatively high stiffness and are useful for making articles where inherent rigidity is required. Copolymerisation of ethylene with higher 1-olefins (e.g. butene, hexene or octene) can provide a wide variety of copolymers differing in density and in other important
15 physical properties. Particularly important copolymers made by copolymerising ethylene with higher 1-olefins with the catalysts of the invention are the copolymers having a density in the range of 0.91 to 0.93. These copolymers which are generally referred to in the art as linear low density polyethylene, are in many respects similar to
20 the so called low density polyethylene produced by the high pressure free radical catalysed polymerisation of ethylene. Such polymers and copolymers are used extensively in the manufacture of flexible blown film.

 Propylene polymers produced by the process of the invention include propylene homopolymer and copolymers of propylene with less than 50 mole % ethylene or other alpha-olefin such as butene-1, pentene-1, 4-methylpentene-1, or hexene-1, or mixtures
25 thereof. Propylene polymers also may include copolymers of propylene with minor amounts of a copolymerizable monomer. Typically, most useful are normally-solid polymers of propylene containing polypropylene crystallinity, random copolymers of propylene with up to about 10 wt.% ethylene, and impact copolymers containing up to about 20 wt.% ethylene or other alpha-olefin. Polypropylene homopolymers may
30 contain a small amount (typically below 2 wt.%) of other monomers to the extent the properties of the homopolymer are not affected significantly.

 Propylene polymers may be produced which are normally solid, predominantly

isotactic, poly α -olefins. Levels of stereorandom by-products are sufficiently low so that useful products can be obtained without separation thereof. Typically, useful propylene homopolymers show polypropylene crystallinity and have isotactic indices above 90 and many times above 95. Copolymers typically will have lower isotactic indices, typically above 80-85.

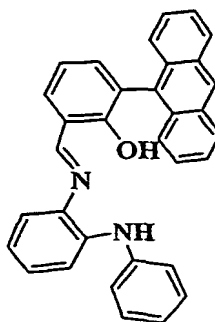
Depending upon polymerisation conditions known in the art, propylene polymers with melt flow rates from below 1 to above 1000 may be produced in a reactor. For many applications, polypropylenes with a MFR from 2 to 100 are typical. Some uses such as for spunbonding may use a polymer with an MFR of 500 to 2000.

Depending upon the use of the polymer product, minor amounts of additives are typically incorporated into the polymer formulation such as acid scavengers, antioxidants, stabilizers, and the like. Generally, these additives are incorporated at levels of about 25 to 2000 ppm, typically from about 50 to about 1000 ppm, and more typically 400 to 1000 ppm, based on the polymer.

In use, polymers or copolymers made according to the invention in the form of a powder are conventionally compounded into pellets. Examples of uses for polymer compositions made according to the invention include use to form fibres, extruded films, tapes, spunbonded webs, moulded or thermoformed products, and the like. The polymers may be blown into films, or may be used for making a variety of moulded or extruded articles such as pipes, and containers such as bottles or drums. Specific additive packages for each application may be selected as known in the art. Examples of supplemental additives include slip agents, anti-blocks, anti-stats, mould release agents, primary and secondary anti-oxidants, clarifiers, nucleants, uv stabilizers, and the like. Classes of additives are well known in the art and include phosphite antioxidants, hydroxylamine (such as N,N-dialkyl hydroxylamine) and amine oxide (such as dialkyl methyl amine oxide) antioxidants, hindered amine light (uv) stabilizers, phenolic stabilizers, benzofuranone stabilizers, and the like. Various olefin polymer additives are described in U.S. patents 4,318,845, 4,325,863, 4,590,231, 4,668,721, 4,876,300, 5,175,312, 5,276,076, 5,326,802, 5,344,860, 5,596,033, and 5,625,090.

Fillers such as silica, glass fibers, talc, and the like, nucleating agents, and colourants also may be added to the polymer compositions as known by the art.

EXAMPLES

Example 1 - Synthesis of 1-[(3-An-2-OH-C₆H₃)CH=N]-2-PhNH-C₆H₄ (I)

Absolute ethanol (15 ml) was added to a mixture of 3-anthracenyl-2-hydroxybenzaldehyde (1.00 g, 3.35 mmol) and *n*-phenyl-1,2-phenylenediamine (0.62 g, 3.35 mmol). After the addition of a few drops of formic acid, the yellow suspension was
 5 refluxed for 18 hours. Upon cooling to room temperature, the suspension was filtered and the yellow solid washed with cold pentane and dried under vacuum overnight.
 (1.06g, 68%)

Mass Spec: (EI, *m/z*) 464 [*M*]⁺.

¹H NMR: (250MHz, CDCl₃, 298K) δ 6.07 (s, 1H, *NH*), 6.90-8.55 (m, 21 H, *Ar-H*),
 10 8.84 (s, 1H, *N=CH*), 13.04 (s, 1H, *OH*).

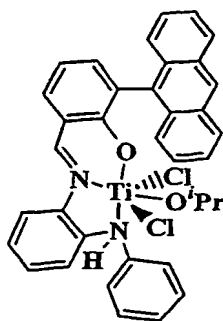
¹³C NMR: (63MHz, CDCl₃, 298K) δ 115.11, 118.92, 119.34, 119.84, 120.07, 120.41, 122.31, 125.12, 125.60, 126.46, 126.91, 127.19, 127.92, 128.62, 129.21, 130.37, 131.53, 132.12, 132.53, 136.68, 137.00, 138.13, 141.71, 159.05 (*Ar-C*), 162.94 (*N=CH*).

15 **Infra red:** (NaCl, cm⁻¹) 1606s (C=N), 3405w (N-H).

Elemental Analysis: C₃₃H₂₄N₂O found (calculated)

%C = 85.37 (85.34), %H = 5.09 (5.17), %N = 5.94 (6.03).

Example 2 - Synthesis of {1-[(3-An-2-O-C₆H₃)CH=N]-2-PhNH(C₆H₄)Ti(O^{*i*}Pr)Cl₂ (II)}



A solution of $\text{Ti}(\text{O}^i\text{Pr})_2\text{Cl}_2 \cdot 0.5\text{THF}$ (0.15 g, 0.54 mmol) in THF (20 ml) was cooled to -78°C . It was added to a solution of compound I (0.25 g, 0.54 mmol) in THF (20 ml) at -78°C , and allowed to warm to room temperature and stirred for 18 hours. Volatiles were removed under vacuo. Extraction into MeCN and recrystallisation from hot MeCN

5 solution yielded red crystals of compound II. (0.15g, 14%). The proposed structure (above) was confirmed by X-ray crystallography of suitably grown crystals.

^1H NMR: (250MHz, CDCl_3 , 298K) δ 0.04 (d, 6H, $^3J(\text{HH})$ 6.2, $\text{OCH}(\text{CH}_3)_2$), 4.32 (sept, 1H, $^3J(\text{HH})$ 6.2, $\text{OCH}(\text{CH}_3)_2$), 6.81 – 8.46 (m, 21H, *Ar-H*), 8.95 (s, 1H, $\text{N}=\text{CH}$).

^{13}C NMR: (125MHz, CDCl_3 , 298K) δ 22.25 ($\text{OCH}(\text{CH}_3)_2$), 22.39 ($\text{OCH}(\text{CH}_3)_2$), 85.68
10 ($\text{OCH}(\text{CH}_3)_2$), 117.14, 122.09, 122.18, 122.78, 123.78, 124.09, 124.96, 125.11, 125.17, 125.44, 125.70, 126.01, 126.17, 126.46, 126.68, 126.83, 127.87, 127.91, 128.23, 128.41, 129.03, 129.25, 130.19, 130.33, 131.31, 131.39, 131.96, 135.44, 139.98, 140.46, 142.97, 143.70, 161.23 (*Ar-C*), 159.94 ($\text{N}=\text{CH}$).

Infra red: (NaCl , cm^{-1}) 1613s ($\text{C}=\text{N}$), 3180w (N-H).

15 **Elemental Analysis:** $\text{C}_{36}\text{H}_{30}\text{N}_2\text{O}_2\text{TiCl}_2$ found (calculated)

%C = 67.39 (67.42), %H = 4.64 (4.68), %N = 4.30 (4.36).

Examples 3 – 11 : Polymerisation results

Polymerisation Method A

The catalyst II was charged into a Schlenk tube and dissolved in 100 ml of toluene, then
20 the activator solution (600 equivalents MAO) was added. The Schlenk tube was purged with ethylene and the contents were mechanically stirred and maintained under 1 bar (absolute) of ethylene throughout the experiment. The polymerisation was terminated by the addition of aqueous hydrogen chloride followed by the addition of methanol. The produced solid polyethylene was filtered off, washed with methanol and dried under
25 vacuum at 50°C .

Polymerisation Method B

A 1 litre reactor was baked out under a nitrogen flow for at least 1 hour at $>85^\circ\text{C}$. The reactor was then cooled to 50°C . Isobutane (0.5 litre) and triisobutylaluminium were then added and the reactor was boxed in nitrogen. The alkyl aluminium was allowed to
30 scavenge for poisons in the reactor for at least 1 hour. The reactor was allowed to equilibrate at the desired temperature and ethylene was introduced into the reactor until a predetermined over-pressure was achieved, then the catalyst solution (7.8 mmol of II,

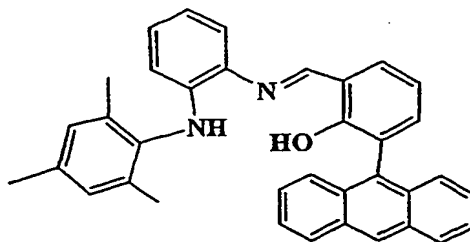
600 equivalents MAO in toluene) was injected under nitrogen. The reactor pressure was maintained constant throughout the polymerisation run by computer controlled addition of additional ethylene. The polymerisation time was 1 hour. Upon termination of the run the reactor contents were isolated, washed with acidified methanol (50ml

5 HCl/2.5l methanol) and water/ethanol (4:1 v/v) and dried under vacuum, at 40°C, for 16 hours.

The results of the polymerisation tests are summarised in the following Table;

Example	Polymerisation method	T/°C	C2/Bar	PE/g	Activity g/mmol[Ti].h.b
3	A	22	1	3.82	490
4	A	50	1	5.18	664
5	B	40	8	15.47	248
6	B	50	8	23.05	369
7	B	60	8	17.55	281
8	B	70	8	6.38	102
9	B	50	1	3.33	427
10	B	50	4	11.29	362
11	B	50	6	14.39	307

10 **EXAMPLE 12 – Synthesis of 1-[(3-An-2-OH-C₆H₃)CH=N]-2-[(2,4,6-Me₃-C₆H₂)NH]-C₆H₄**



Absolute ethanol (15 mL) was added to a mixture of 3-anthracenyl-2-hydroxybenzaldehyde (1.00 g, 3.35 mmol) and *N*-mesityl-1,2-phenylenediamine (0.76

15 g, 3.35 mmol). After the addition of a few drops of formic acid, the solution was

refluxed for 18 hours. Upon cooling to room temperature, the suspension was filtered and the yellow solid was washed with cold pentane and dried under vacuum overnight (1.10 g, 65 %).

Mass Spectrum Data : (EI, m/z) 506 [M⁺]

5 ¹H NMR data : (250 MHz, CDCl₃, 298K) δ 2.05 (s, 6H), 2.30 (s, 3H), 5.58 (s, 1H), 6.16 – 8.68 (m, 18H), 8.91 (s, 1H), 13.11 (s, 1H)

¹³C NMR data : (101 MHz, CDCl₃, 298 K) δ 18.2, 20.9, 112.0, 117.5, 118.2, 119.3, 112.0, 124.9, 125.1, 125.4, 125.6, 126.3, 126.5, 126.6, 126.8, 127.2, 128.4, 128.6, 129.1, 130.2, 130.4, 131.5, 132.2, 132.5, 134.6, 134.8, 135.8, 136.2, 136.5, 141.0,

10 159.0, 162.0, 162.0

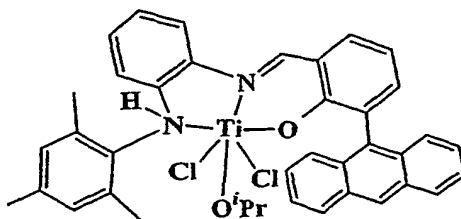
Selected infrared data : (NaCl, cm⁻¹) 1606s (C=N), 3405w (N-H)

Elemental analysis C₃₆H₃₀N₂O, found (calculated)

%C = 85.25 (85.38), %H = 6.07 (5.93), %N = 5.46 (5.53)

EXAMPLE 13 – Synthesis of {1-[(3-An-2-OH-C₆H₃)CH=N]-2-[(2,4,6-Me₃-

15 C₆H₂)NH]-C₆H₄}Ti(OⁱPr)Cl₂



To a solution of Ti(OiPr)₂Cl₂·0.5THF (0.11 g, 0.39 mmol) in THF (20 mL) at –78°C was added a solution of the compound prepared in Example 12 (0.20 g, 0.39 mmol) in THF (20 mL) at –78°C. The mixture was allowed to warm to room temperature and stirred for 18 hours. The volatile components were removed in vacuo. Extraction into pentane followed by concentration and filtration gave a deep red solution. On standing at –20°C red crystals of the title compound were obtained. (0.16 g, 59 %)

¹H NMR data : (250 MHz, CDCl₃, 298K) δ 0.18 (d, 6H), 3.95 (sept, 1H), 2.00 (s, 3H), 2.21 (s, 6H), 6.80 – 8.46 (m, 18H), 9.07 (s, 1H)

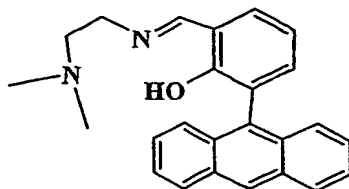
25 ¹³C NMR data : (101 MHz, CDCl₃, 298 K) δ 20.6, 22.6, 25.3, 86.2, 116.8, 122.0, 125.0, 125.1, 125.3, 125.6, 126.4, 126.8, 127.2, 128.0, 128.2, 128.6, 128.8, 129.1, 129.5, 129.8, 130.4, 130.7, 130.9, 131.4, 132.2, 135.5, 135.7, 139.1, 139.5, 139.9, 142.9, 162.3, 159.4

Selected infrared data : (NaCl, cm⁻¹) 1559s (C=N), 3152w (N-H)

Elemental analysis $C_{39}H_{36}N_2O_2TiCl_2$ found (calculated)

%C = 68.29 (68.54), %H = 5.13 (5.27), %N = 4.24 (4.10)

EXAMPLE 14 – Synthesis of (3-An-2-OH- C_6H_3)CH=NCH₂CH₂NMe₂



- 5 Absolute ethanol (20 mL) was added to a mixture of 3-anthracenyl-2-hydroxybenzaldehyde (1.09 g, 3.64 mmol) and *N,N*-dimethylethylenediamine (0.4 mL, 3.64 mmol). After the addition of a few drops of formic acid, the solution was refluxed for 18 hours. Upon cooling to room temperature, the product was crystallized from ethanol. After filtration the yellow solid was washed with cold pentane and dried under vacuum overnight (0.66 g, 49 %).

Mass Spectrum Data : (EI, *m/z*) 368 [M⁺]

¹H NMR data : (250 MHz, CDCl₃, 298K) δ 2.25 (s, 6H), 2.58 (t, 2H), 3.69 (t, 2H), 7.10 – 8.06 (m, 12H), 8.51 (s, 1H)

¹³C NMR data : (101 MHz, CDCl₃, 298 K)

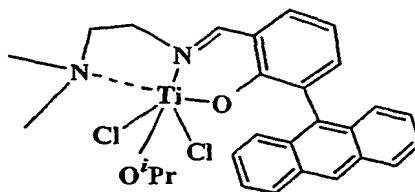
- 15 δ 45.4, 57.1, 59.5, 118.4, 119.0, 120.2, 125.0, 125.4, 126.0, 126.6, 126.9, 127.4, 128.5, 130.4, 131.4, 131.5, 135.5, 159.6, 162.6, 165.8

Selected infrared data : (NaCl, cm⁻¹) 1627s (C=N)

Elemental analysis $C_{25}H_{24}N_2O$ found (calculated)

%C = 81.58 (81.52), %H = 6.58 (6.52), %N = 5.61 (7.61)

- 20 **EXAMPLE 15 – Synthesis of [(3-An-2-OH- C_6H_3)CH=NCH₂CH₂NMe₂]Ti(O^{*i*}Pr)Cl₃**



- To a solution of Ti(O^{*i*}Pr)₂Cl₂·0.5THF (0.19 g, 0.68 mmol) in THF (20 mL) at –78°C was added a solution of the compound prepared in Example 14 (0.25 g, 0.68 mmol) in THF (20 mL) at –78°C. The mixture was allowed to warm to room temperature and stirred for 18 hours. The volatile components were removed in vacuo. Extraction into acetonitrile followed by concentration and filtration gave a deep red solution. On

standing at room temperature red crystals of the title compound were obtained. (0.25 g, 61 %) The proposed structure (above) was confirmed by X-ray crystallography of suitably grown crystals.

¹H NMR data : (250 MHz, CDCl₃, 298K) δ 0.06 (d, 3H), 0.52 (d, 3H), 1.55 (s, 3H), 1.71 (s, 3H), 2.23 (m, 1H), 2.81 (m, 1H), 3.56 (m, 1H), 3.85 (m, 1H), 4.04 (sept, 1H), 6.98 – 8.13 (m, 12 H), 8.39 (s, 1H)

¹³C NMR data : (101 MHz, CDCl₃, 298 K) δ 23.4, 24.2, 50.3, 52.5, 56.1, 60.0, 81.3, 119.7, 120.3, 124.4, 125.4, 125.5, 125.6, 125.7, 126.1, 126.2, 127.4, 127.5, 127.7, 127.8, 126.1, 129.3, 133.7, 135.0, 137.5, 138.2, 162.5

10 Selected infrared data : (NaCl, cm⁻¹) 1617s (C=N)

Elemental analysis C₂₈H₃₀N₂O₂TiCl₂ found (calculated)

%C = 57.84 (57.80), %H = 5.36 (5.33), %N = 4.80 (4.81)

EXAMPLE 16 : Ethylene Polymerisation

Ethylene polymerization was conducted according to Method A (described above) using 16 micromoles of the complex prepared in Example 13 in place of catalyst II at 1 bar ethylene pressure and at room temperature. 0.94 g of polyethylene was isolated, resulting in an activity of 62 g/mmol.h.bar. GPC analysis showed Mw = 128 000, Mn = 50 000, Mw/Mn = 2.6, Mpk = 80000

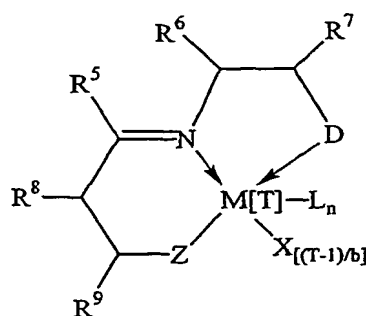
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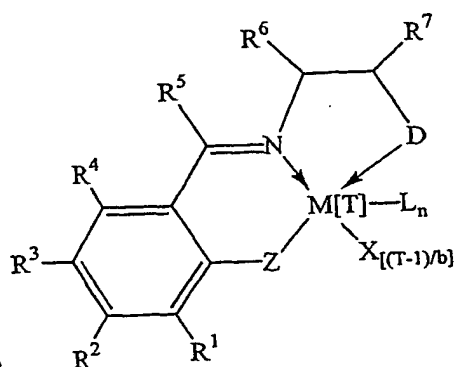
Claims:

1. A complex having the formula (I)



Formula (I)

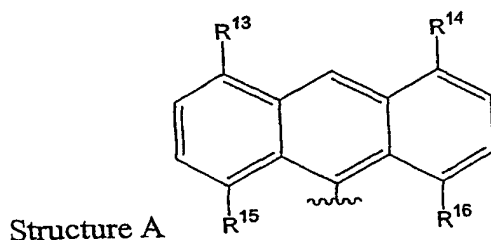
- wherein M is a transition metal, lanthanide or actinide and T is its oxidation state; X represents an atom or group covalently or ionically bonded to M; b is the valency of the atom or group X; L is a group datively bound to M, and n is from 0 to 4; Z is oxygen, sulphur or a group represented by NR¹⁰ or PR¹⁰; D is a group datively bound to M, comprising a neutral donor selected from NR¹¹R¹², PR¹¹R¹², OR¹¹ or SR¹¹; and R⁵ to R¹² are all independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl or SiR'₃ where each R' is independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl, and any two or more of each R⁵ to R¹² may be linked to form cyclic substituents
2. A complex as claimed in Claim 1 having the formula (II)



Formula (II)

wherein R^5 to R^7 , M, T, L, n, b, X, Z and D are as defined in Claim 1, and R^1 to R^4 are each independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl or SiR'_3 where each R' is independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl, and any two or more of R^1 to R^7 and R^{10} to R^{12} may be linked to form cyclic substituents.

3. A complex as claimed in Claim 2 wherein R^1 is a cyclic hydrocarbyl group.
4. A complex as claimed in Claim 2 wherein R^1 is a polycyclic hydrocarbyl group.
5. A complex as claimed in any one of Claims 2 to 4 wherein R^1 is unsubstituted or substituted with one or more $\text{C}_1\text{-C}_6$ alkyl groups and is selected from anthracenyl, naphthyl or triptycenyl.
6. A complex as claimed in any one of Claims 2 to 4 wherein R^1 is unsubstituted or substituted with one or more $\text{C}_1\text{-C}_6$ alkyl groups and is phenanthrenyl.
7. A complex as claimed in Claim 2 wherein R^1 has the following Structure A:



Structure A

where R^{13} to R^{16} are each independently hydrogen or methyl.

8. A complex as claimed in any one of the preceding Claims wherein M is Ti[II], Ti[III], Ti[IV], Fe[II], Fe[III], Co[II], Co[III], Ni[II], Cr[II], Cr[III], Mn[II], Mn[III], Mn[IV], Ta[II], Ta[III], Ta[IV], Rh[II], Rh[III], Y[II], Y[III], Sc[II],

Sc[III], Ru[II], Ru[III], Ru[IV], Pd[II], Zr[II], Zr[III], Zr[IV], Hf[II], Hf[III], Hf[IV], V[II], V[III], V[IV], Nb[II], Nb[III], Nb[IV] or Nb[V].

9. A complex as claimed in any one of the preceding Claims wherein Z is oxygen.

5 10. A complex as claimed in any one of the preceding Claims wherein D is $PR^{11}R^{12}$ and R^{11} and R^{12} are both phenyl.

11. A complex as claimed in any one of Claims 1 to 9 wherein D is $NR^{11}R^{12}$ and R^{11} and R^{12} are each independently a hydrogen or hydrocarbyl group.

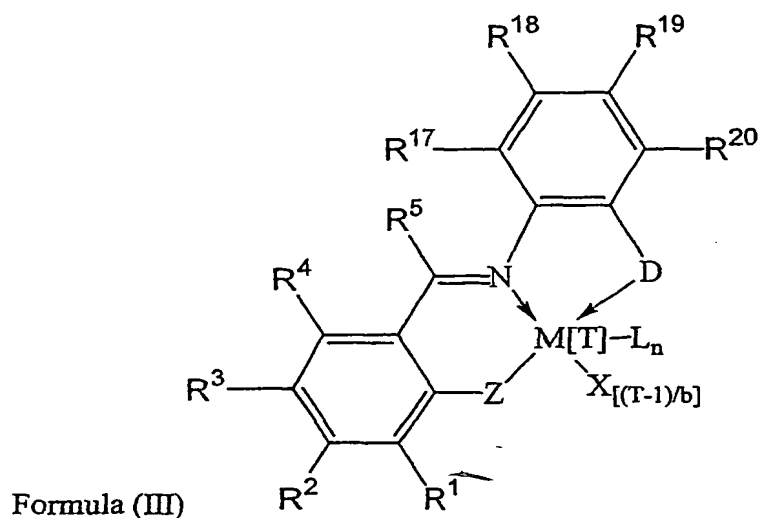
12. A complex as claimed in any one of the preceding Claims wherein X is
10 selected from halide, hydride, hydrocarbyloxy and hydrocarbyl.

13. A complex as claimed in any one of the preceding Claims wherein the group L is selected from an ether, an alcohol and a primary, secondary or tertiary amine.

14. A complex as claimed in Claim 7 wherein, M is Ti(IV), Z is oxygen, R^1 is Structure A, all of R^2 to R^7 are hydrogen, R^{13} to R^{16} are all methyl and D is NMe_2 ,
15 the three X groups consist of two Cl groups and one O^iPr group, and L is tetrahydrofuran.

15. A complex as claimed in any one of Claims 2 to 14 wherein at least two of R^2 to R^7 are linked to form a cyclic substituent.

16. A complex as claimed in any one of Claims 2 to 15 wherein R^6 and R^7 are
20 linked to form a cyclic substituent to provide complex of Formula (III):



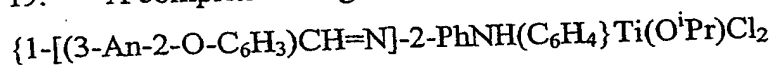
wherein R^{17} to R^{20} are each independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted

heterohydrocarbyl or SiR'_3 where each R' is independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl, and any two or more of the R groups may be linked to form cyclic substituents.

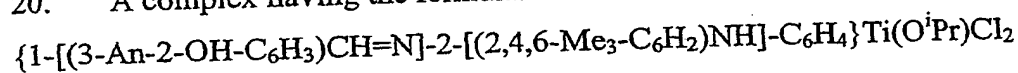
5 17. A complex as claimed in Claim 16 wherein R2 to R5 and/or R17 to R20 are each independently selected from hydrogen or hydrocarbyl.

18. A complex as claimed in Claim 16 or 17 wherein M is Ti(IV), Z is oxygen, R^1 is Structure A, R^2 to R^5 and R^{13} to R^{20} are all hydrogen and D is NHPH, the three X groups consist of 2 Cl groups and one OⁱPr group, and L is tetrahydrofuran.

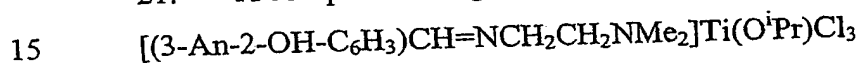
10 19. A complex having the formula:



20. A complex having the formula:



21. A complex having the formula:



22. A polymerization catalyst comprising the complex claimed in any one of the preceding Claims.

23. A polymerization catalyst comprising (a) the complex claimed in any one of Claims 1 to 22 and (b) an effective amount of at least one activator compound.

20 24. A polymerization catalyst as claimed in Claim 23 wherein the activator compound is selected from organoaluminium compounds and hydrocarbylboron compounds.

25 25. A polymerization catalyst as claimed in Claim 23 wherein the activator compound is a salt of a cationic oxidising agent and a non-coordinating compatible anion.

26. A polymerization catalyst as claimed in Claim 23 wherein the activator compound is an alkylalumoxanes, preferably methylalumoxane (MAO).

27. A process for the polymerisation and copolymerisation of 1-olefins, comprising contacting the monomeric olefin under polymerisation conditions with the polymerisation catalyst claimed in any one of Claims 22 to 26.

30 28. A process as claimed in Claim 27 wherein the monomer comprises one or more of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methylpentene-1, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-

tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, and 1-eicosene.

29. A process as claimed in Claim 27 wherein the monomeric olefin is copolymerised with monomer selected from methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, styrene, 1.4-pentadiene, 1,5-hexadiene, cyclopentadiene, ethylene norbornadiene.

30. Polyolefins whenever prepared by the process of any one of Claims 27 to 29.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 02/02144

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07F7/00 C08F10/00 C08F4/642

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

16 August 2002

Date of mailing of the international search report

28/08/2002

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INTERNATIONAL SEARCH REPORT

Int ernational Application No

PCT/GB 02/02144

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X	WO 00 59954 A (BASF AG ;CHRISTIE DAVID (DE); CLAVERIE JEROME (FR); KANAGASABAPATH) 12 October 2000 (2000-10-12) page 4, line 1 - line 22 page 22 -page 31	1, 9, 22-30
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X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; YOUSAF, MUHAMMAD ET AL: "Synthesis, characterization and catalytic applications of tridentate Schiff base derivatives of bis and mono(cyclopentadienyl)lanthanocen e complexes" retrieved from STN Database accession no. 134:5193 XP002209534 abstract & CHINESE JOURNAL OF CHEMISTRY (2000), 18(5), 740-744 ,	1, 2, 8, 9, 12, 13, 22, 30

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INTERNATIONAL SEARCH REPORT

Int ernational Application No
PCT/GB 02/02144

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; YOUSAF, MUHAMMAD ET AL: "Polymerization of MMA catalyzed by different novel mixed ligand lanthanocene {(Cp)(Cl)Ln Schiff-base(THF)}, (COT)Ln(methoxyethylindenyl)(THF)/Al(i-Bu) 3 systems" retrieved from STN Database accession no. 134:5194 XP002209535 abstract & CHINESE JOURNAL OF CHEMISTRY (2000), 18(5), 759-763 ,</p>	<p>1,2,8,9, 12,13, 22,30</p>
P,X	<p>WO 01 44324 A (ITTEL STEVEN DALE ;DU PONT (US); WANG YING (US)) 21 June 2001 (2001-06-21) page 28 -page 36</p>	<p>1-30</p>

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Int ernational Application No

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